

CHAPTER - 2

CHARACTERIZATION TECHNIQUES

Synthesis, growth, characterization and application of the single crystals have attracted materials scientist in the field of laser and optoelectronic devices. Characterization of a crystal essentially consists of an evaluation of its chemical composition, structure, defects and study of their optical properties. The determination of the crystal structure is an indispensable part of the characterization of materials, chiefly the identification of the chemical species. This will assist, to make rapid progress in the growth process and also improve the quality of the crystal [43]. In order to estimate the perfection of the grown crystals an assessment technique is required, and post growth analysis provides information on the process that occurred during crystal growth. As the technology of instrumentation analysis has improved with the advent of analytical balances, automated titrations and computer controlled instruments, the speed, accuracy and precision of the characterization techniques have improved. In the present work, the single crystals of and semiorganic impurity doped KDP crystals have been analyzed. There are number of experimental techniques used in the present investigation to characterize the properties of the grown single crystals such structural (single crystal XRD) optical (UV-Visible), vibrational (FT-IR/Raman), and dielectric measurements.

2.1 Single crystal X-ray diffraction

Single crystal X-ray diffraction is the powerful tool used to determine the structure of single crystalline solids. A single crystal is defined as a sample that has the unit cells that are exactly the same and are all lined up with an identical

orientation. The accurate determination of lattice parameters provides an important basis in understanding various properties of the materials. The different types of defects may be co-existent in crystalline materials; hence the problems that arise are of separation of different types of defects and identification and quantitative estimation of the extent and distribution of each type of defect. The various factors affecting the diffraction intensities can be grouped into a single expression for use in calculating the relative intensities of reflections. X-Ray diffraction is an important technique in material characterization. It is useful for both powder as well as pellet analysis.

When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. Molybdenum is the most common target material used for single-crystal diffraction, with MoK α radiation (0.7107 Å). These X-rays are collimated and directed onto the sample (Bonse and Hart 1965) [44]. X-Ray Diffraction patterns are used to establish the atomic arrangement or structure of the materials because the d spacing of diffraction planes is of the order of X-Ray wavelength λ , the various orders n of reflection occur only at the precise values of angle θ , which satisfies the Bragg equation given by $n\lambda = 2d\sin\theta$ [45] where d is the interplanar spacing of the incident plane, λ is the wavelength of X-rays and n is a positive integer. The intensity of the diffracted rays depends on the arrangement and nature of atoms in the crystal. Collection of intensities of a full set of planes in the crystal contains the complete structural information about the molecule.

When the geometry of the incident X-rays impinging the sample surface as shown in **Fig. 2.1**, constructive interference occurs. A detector records and processes

this X-ray signal and converts the signal to a count rate. Single crystal diffractometers use either 3- or 4-circle goniometers. These circles refer to the four angles (2θ , χ , ϕ , and Ω) that define the relationship between the crystal lattice, the incident ray and detector [46]. Samples are mounted on thin glass fibers which are attached to brass pins and mounted onto goniometer heads. Single crystal of suitable size was cut and mounted on the X-ray goniometer. The crystal was optically centered at the sphere of confusion using the built in tele-microscope. 25 reflections were collected from different zones of the reciprocal lattice using random search procedure. The reflections were indexed using the method of short vectors followed by least square refinements. The unit cell parameters thus obtained were transformed to correct Bravais cell.

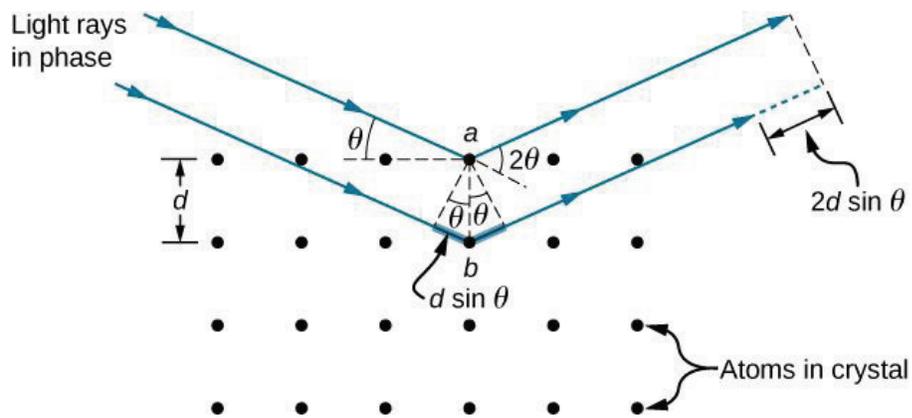


Fig. 2.1 Diffraction in crystal lattices

Single crystal X-ray diffraction is most commonly used for precise determination of a unit cell, including cell dimensions and positions of atoms within the lattice.

2.2 Fourier Transform Infrared Spectroscopy

Fourier transform Infrared spectroscopy is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation. This technique is one of the most important and widely used spectroscopic techniques for analysing quantitatively the structural units of the unknown compounds. It helps to identify the functional units, internal structure of the molecules and nature of the chemical bonds of a compound. **Fig. 2.2** shows the schematic of FT-IR spectrometer. Radiations containing all wavelengths ($4000\text{-}400\text{ cm}^{-1}$) is split into two beams. One beam is of fixed length and the other is of movable length. The varying distances between two path lengths result in consecutive constructive and destructive interferences hence variations in intensities: an interferogram. Fourier transformation converts this interferogram from the time domain to the familiar form of frequency domain. Smooth and continuous variation in the position of mirror B can be adjusted. It is an ideal analytical technique for the study of condensed phase materials, if chemical specificity and selectivity are sought. A complementary technique to Raman spectroscopy, FTIR has gained widespread acceptance as a characterization tool primarily due to its universality and versatility. The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule [47]. As such, the IR spectrum can be

used as a fingerprint for identification by the comparison of the spectrum from an "unknown" with previously recorded reference spectra.

Absorption of infrared radiations is confined largely to molecular species for which small energy differences exist between various vibrational and rotational states. When the frequency of the incident radiation coincides with the vibrational frequency of the molecules, absorption of energy takes place. When the molecules return from the excited state to the ground state the absorbed energy is released resulting in distinct peaks in the IR spectrum. These IR absorption bands reveal the state of the molecules present in the sample. In this study, the KBr pellet method was used to record the IR spectra of the grown crystals, where crushed powder of the grown crystals was mixed with KBr and pelletised using a hydraulic press. In Fourier Transform IR spectroscopy, the infrared radiation is analyzed by means of a scanning interferometer. The interferogram containing all the information is constructed into the spectrum with the help of the mathematical programming called Fourier Transformation.

The FTIR spectra of pure and semiorganic impurity added (0.2, 0.4, 0.6, 0.8 and 1 mole%) KDP crystals grown in the present study have been recorded in the above mentioned range. Using Perkin Elmer Fourier transform infrared spectrometer (Model : Spectrum RXI) using KBr pellet method. The spectra were used to analyze the presence of different constituents and their bonding properties qualitatively [48].

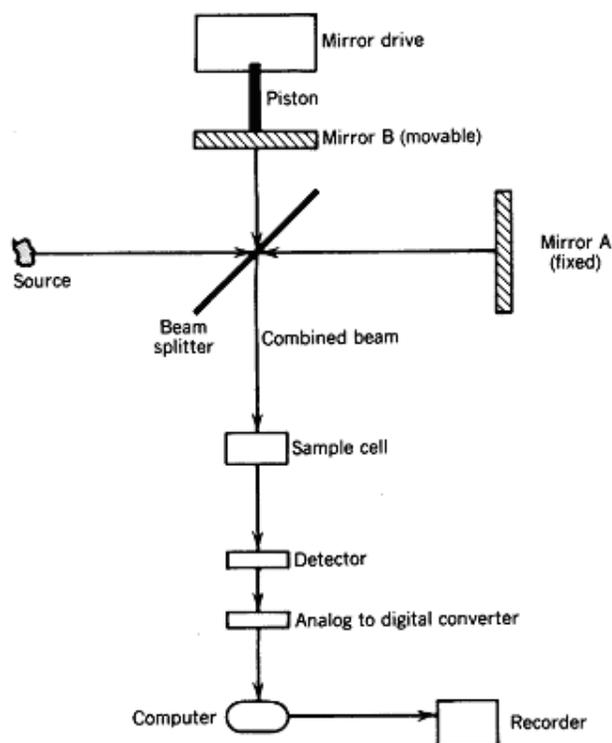


Fig. 2.2 Schematic of FT-IR Spectrometer

Fourier transformation at successive points throughout this variation gives rise to complete IR spectrum. The pellet technique depends on the fact that dry powdered potassium bromide can be compacted under pressure 10,000 psi using special dyes to form transparent disks (Silverstein et al 1981) [49].

2.3 Laser Raman spectroscopy

Yet another extremely useful spectroscopic tool is Raman microspectroscopy, because the vibrational spectra acquired can be used to detect molecular bonds and spot the differences in local environments. This is because specific vibrational frequencies are possessed by the bonds formed between atoms. And these frequencies correspond to an atom's strength and mass of the bond between the atoms. Hence, complex molecules show many peaks and can be quickly identified by

the "fingerprint" or pattern produced by those peaks. For one and two-dimensional materials, this is particularly useful because the sampling area is restricted by the size of the laser spot, and it is capable of detecting the differences in local environments.

Raman spectroscopy concerns with the scattering of radiation by the sample rather than an absorption process. This is Raman scattering, based on the principle of inelastic scattering of photons by molecules. For a transition to be Raman active there must be a change in polarizability of the molecule. Diatomic molecules do not possess a permanent electric dipole, and so they are undetectable. The energy of the exciting radiation will determine as to which type of transition occurs. The energy of the rotational transitions are lower than the vibrational transitions (Clark 2007) [50].

The experimental setup that was used for the present investigation comprised of a He-Ne excitation source at the wavelength of 632.8 nm and Argon 488 nm coupled with a Labram2HR800 micro Raman spectrometer. The incident laser was focused to a spot size of 2 μm and power of the laser was 2 mW with high stability confocal Microscope for Micro Raman 10x, 50x, 100x objective lens. The spectral resolution is of the order of 1 cm^{-1} and the setup is shown in **Fig. 2.3** is an optical diagram of a microspectrometer configured for Raman microspectroscopy.. In the case of Raman microspectroscopy, the optical diagram is somewhat different which is attributed to the nature of these types of experiments. Through incident illumination, the laser is focused onto a sample and the Raman scattered light is collected and imaged onto the spectrophotometer's entrance aperture, and this is followed by collecting a Raman microspectra.

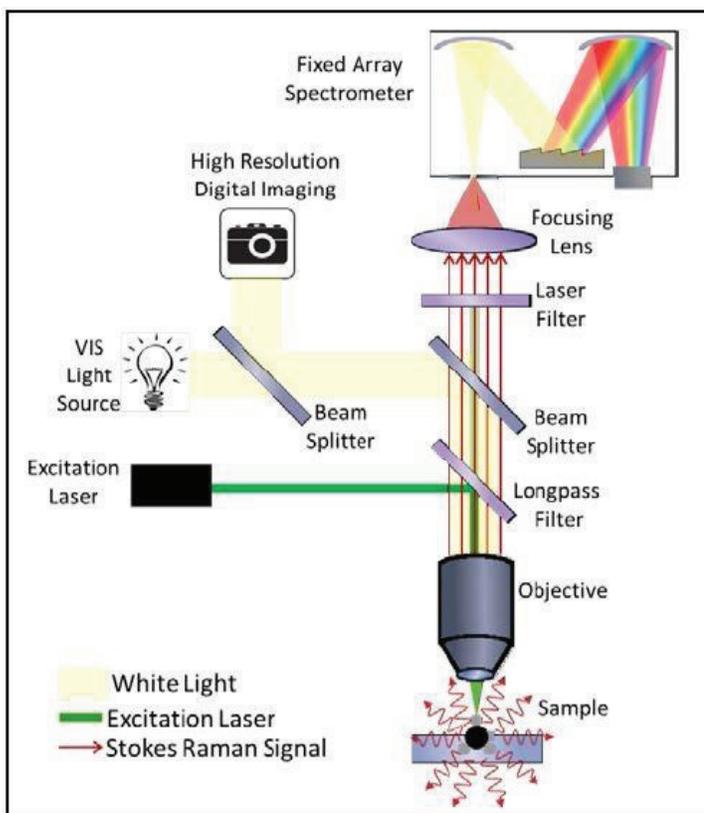


Fig. 2.3 Optical diagram of Raman microspectra

2.4 UV-Vis -NIR spectral measurements

UV-Vis spectroscopy is one of the most important analytical and characterization techniques which is useful in characterizing the absorption, transmission, and reflectivity of a variety of technologically important materials. The Ultraviolet-Visible-Near infrared (UV-Vis-NIR) spectroscopy measures the absorption or emission of radiation associated with the changes in the spatial distribution of electrons in atoms and molecules. In practice, the electrons involved are usually the valence or the bonding electrons, which can be excited by absorption of UV or visible or near IR radiation [51]. The quantity of absorption depends on the wavelength of the radiation and the structure of the compound. The radiation

absorption is due to the subtraction of energy from the radiation beam when electrons in orbitals of lower energy are excited into orbitals of higher energy. Since this is an electron excitation phenomenon, it is also called as electronic spectroscopy. After the sample absorbs a portion of the incident radiation, the remainder is transmitted on to a detector where it is changed into an electrical signal and displayed after amplification. The transmission spectrum shows what percentage of the incoming light that actually makes it through the sample.

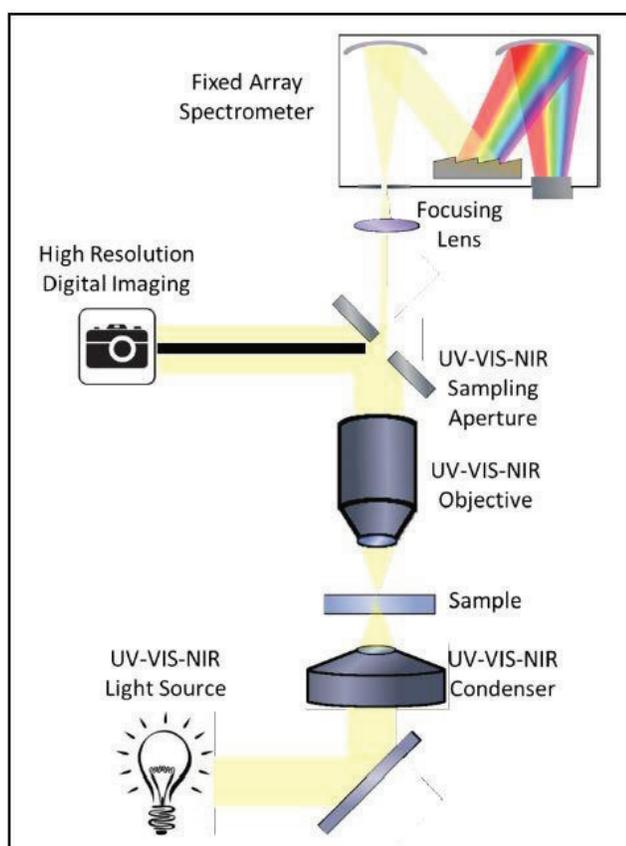


Fig. 2.4 Optical diagram of UV-Vis-NIR spectrometer

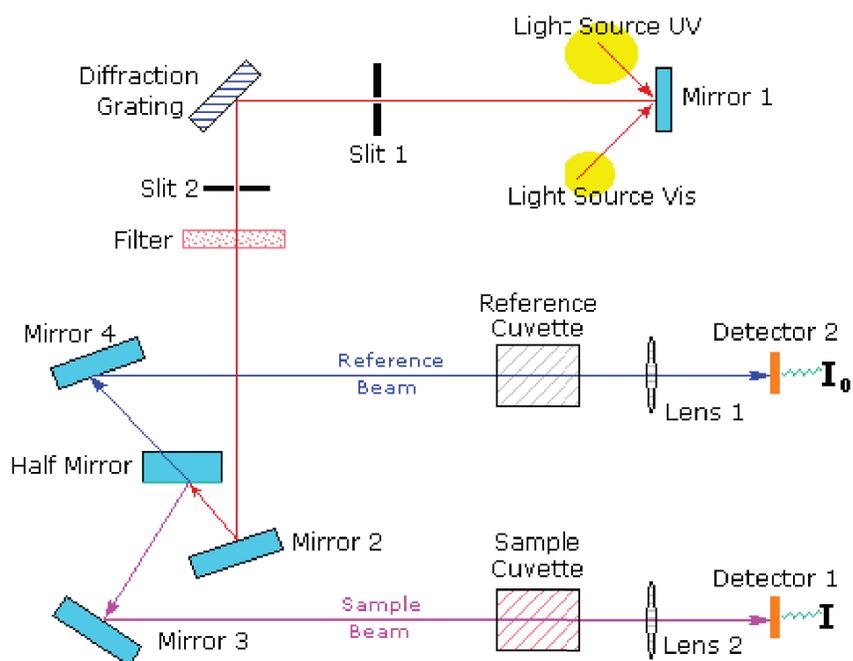


Fig. 2.5 Schematic diagram of UV-Vis-NIR spectrometer

The spectrum of a compound represents a group of either wavelength or frequency, continuously changing over a small portion of the electromagnetic spectrum versus either percent transmission (%T) or absorbance (%A). Transmission spectra are important for any NLO material because, the material can be of use only if it has a wide transparency range to know the suitability for optical applications. In the present study, the UV-Vis-NIR transmission spectra were recorded for the pure and impurity doped KDP single crystals of 2 mm thickness using a Perkin-Elmer Lambda 35 UV-Visible spectrometer in the range 190-1100 nm [52].

2.5 Dielectric measurements

Dielectric measurement is one of the useful characterizations of electrical response of solids. A study of the dielectric properties of solids gives information about the electric field distribution within the solid. The frequency dependence of

these properties gives a great insight into the material's applications. Various polarization mechanisms in solids such as atomic polarization of the lattice, orientational polarization of dipoles and space charge polarizations can be understood by studying the dielectric properties as a function of frequency and temperature for crystalline solids. The frequency dependence of these properties gives insight into the material applications. The dielectric constant is one of the basic electrical properties of solids. The dielectric constant determines the share of the electric stress which is absorbed by the material without any dielectric breakdown. The dielectric loss is a measure of the energy absorbed by a dielectric. The capacitance (C_{crys}) and dielectric loss factor ($\tan \delta$) measurements were carried out to an accuracy of $\pm 2\%$ using an LCR meter (Agilent 4284 A) for a fixed frequency of 1 kHz at various temperatures ranging from 35-150 °C in a way similar to that followed by Mahadevan and his co-workers [53]. Temperature was controlled to an accuracy of $\pm 1^\circ \text{C}$. Impedance measurement can be done with the help of a LCR meter for a varied number of applications. An LCR meter is not only used exclusively for component testing of inductors, resistors and capacitors but also employed in the electrical characterization of gases, chemicals, powders and other dielectric materials.. The samples were prepared and annealed in a way similar to that followed for the resistance measurement. Air capacitances (C_{air}) were also measured for the dimensions equal to that of the crystals. Since the variation of air capacitance with temperature was found to be negligible, air capacitance was measured only at room temperature. Dielectric or an insulating material is a very poor conductor of electric current. When dielectrics are placed in an electric field, practically no current flows in them because, unlike metals, they have no loosely

bound, or free, electrons that may drift through the material. Instead, electric polarization occurs. The positive charges within the dielectric are displaced minutely in the direction of the electric field, and the negative charges are displaced minutely in the direction opposite to the electric field. This slight separation of charge, or polarization, reduces the electric field within the dielectric. The presence of dielectric material affects other electrical phenomena. The force between two electric charges in a dielectric medium is less than it would be in a vacuum, while the quantity of energy stored in an electric field per unit volume of a dielectric medium is greater. The capacitance of a capacitor filled with a dielectric is greater than it would be in a vacuum. The effects of the dielectric on electrical phenomena are described on a large, or macroscopic scale by employing such concepts as dielectric constant, permittivity and polarization. The dielectric constant of the crystal was calculated using the relation

$$\epsilon_r = \frac{C_{crys}}{C_{air}} \quad [54]$$

As the crystal area was smaller than the plate area of the cell, the above relation was modified to account for the air capacitance around the crystal within plate area as

$$\epsilon_r = \left[\frac{A_{air}}{A_{crys}} \right] \left[\frac{C_{crys} - C_{air} \left(1 - \frac{A_{crys}}{A_{air}} \right)}{C_{air}} \right]$$

where C_{crys} is the capacitance with crystal, C_{air} the capacitance of air, A_{crys} is the area of the crystal touching the electrode and A_{air} is the area of the electrode.

2.6 AC Electrical Conductivity

The AC conductivity (ac) was calculated using the relation

$$\sigma_{ac} = \epsilon_0 \epsilon_r \omega \tan \delta$$

where ϵ_0 is the permittivity of free space and is equal to $8.854 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$, ϵ_r is the dielectric constant, $\tan \delta$ is the dielectric loss and ω is the angular frequency.

2.7 Activation energy

The general relation proposed by Arrhenius for the temperature variation of conductivity is given by

$$\sigma = \sigma_0 \exp\left[-\frac{E}{kT}\right] \text{ [55]}$$

where σ_0 is a constant depending on the material, E is the activation energy, T is the absolute temperature and k is the Boltzmann's constant. The above equation can be rewritten as

$$\ln \sigma = \ln \sigma_0 - (kT)$$

A plot of $\ln \sigma$ versus $\frac{1}{T}$ gives $\left\{-\frac{E}{k}\right\}$, the slope and $\ln \sigma_0$ as the intercept. It is customary to plot $\ln \sigma$ versus $1000/T$, from the slope of which the activation energy (E) can be calculated. Values of $\ln \sigma$ were plotted against $\frac{1000}{T}$ for all the grown samples and the AC activation energies were calculated from the slope of the straight line best fitted by least square analysis.

2.8 Ferro electric analysis

Ferroelectrics are characterized the presence of a large remnant polarization the direction of which can be suitably oriented through the application of external electric field. This reversible polarization makes for interesting applications and has been the subject of intense research in the 21st century. Ferroelectrics are both piezoelectric and pyroelectric in nature, in the sense that polarization in ferroelectrics responds to both stress and temperature.

2.8.1 P-E loop tracer

Research in the area of Ferroelectrics is generally driven by the market potential of next generation memories and transducers. It is rapidly emerging in the fields of micro-electro mechanical system (MEMS) technology. Ferroelectric hysteresis loop is the most significant property of ferroelectric materials and measured by the reversal of polarization or switching by an external applied electric field. Since, the P-E loop completely disappears at Curie temperature (T_c) [56]. Therefore, ferroelectric properties such as remnant polarization (P_r), spontaneous polarization (P_s) coercive field (E_c) and Curie temperature (T_c) are determined by hysteresis loops. The schematic diagram of PE loop tracer is shown in **Fig.2.6**.

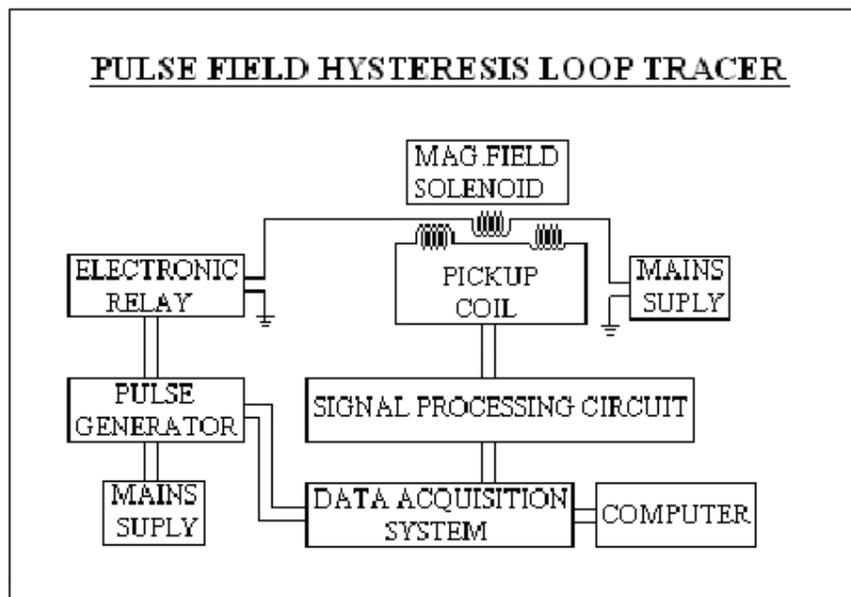


Fig. 2.6 Schematic diagram of PE loop tracer

PE Loop tracer is designed for characterisation of materials such as ferroelectrics. The system measures the hysteresis loops for these materials. The broad specifications and main features are listed here below:

- High voltage power supply with overload protection, Digital potentiometer
- Input 220V Ac, Output 5KV Max Current 20mA, Programmable AC source variable frequency
- Programmable AC source fixed frequency 20Hz to 1kHz,.Current limiting circuit.
- ISA/USB Data acquisition hardware to collect samples from the unit
- Temperature hardware for measuring the temperature of sample bath
- Signal conditioning hardware with unity gain amplifier, Analogue to digital converter hardware
- Integrator selector (for selection of internal reference capacitor and resistance)
- Sample holder Heater 400° C Ramp controller, Temperature measurement hardware
- Minimum Sample Resistance 200 K Ohm, Software for measurement data recording and plotting
- Consumables: Silicon Oil 100ml

2.8.2 Basic theory

The presented measurement technique is based on the Sawyer-Tower method which was introduced to obtain hysteresis loops at ferroelectric samples. The principle is simple when two capacitors are connected in series and AC voltage is applied on both in series, the charge on both will be same. In order to get complete saturation the internal capacitance must be bigger than the sample capacitance. The sample is placed in series with a reference capacitor. The circuit diagram is shown in

Fig 2.7.

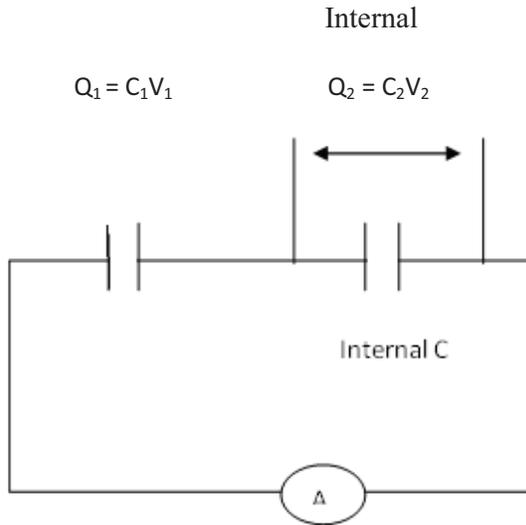


Fig. 2.7 Basic operation of PE loop Tracer

2.8.3 Basic calculation

Based on theory of principal, the charge on both capacitances shall be same if both the capacitors are connected in series and an AC voltage is applied. $Q_1 = Q_2$ [57] which means

$$C_1 V_1 = C_2 V_2 \text{ ----- (A)}$$

The internal capacitor C_2 is known -----1

The total voltage V applied is also known which are $V_1 + V_2$ -----2

If we measure voltage across the internal capacitor i.e. V_2 using a data acquisition card. We can know how much voltage is applied on the sample by subtracting it from the total voltage. Measurement of V_2 by data acquisition card is easy because magnitude of voltage V_2 will be much less than V_1 . This way if all three quantities are known we can find C_1 easily by calculating using above equation (A). We can get a table of Q_1 if we multiply the sinusoidal voltages V_1 with C_1 . This can be calculated simply by mathematical conversation of Q_1 into micro-coulomb and

dividing by area. The second quantity is E which is field in KV/cm. This also can be achieved by converting the sinusoidal voltages V_1 into KV and then dividing by thickness. Hereby the reference capacitor should have at least a capacitance 100 times larger than the capacitance of the sample. Then the voltage drop at the capacitor is negligible and the source voltage is nearly the same as the voltage at the sample. To understand the concept of ferroelectric behaviour of a particular material it is first necessary to discuss the nature of switchable polarization in a ferroelectric material. **Fig. 2.8** shows a typical polarization versus electric field (P-E) hysteresis loop. Within a ferroelectric material dipolar coupling between neighbouring dipoles gives rise to ferroelectric domains. These domains are physical areas within the crystal where all the dipoles are aligned in a particular direction. Individual domains are separated by domain walls. Numerous domains exist within a bulk material possessing random orientation which renders the bulk material inactive. A ferroelectric material can be made to possess functionality through a process known as poling. During poling all the individual domains within a ferroelectric are made to align a particular direction thereby giving the material a bulk polar vector. The processes are described as follows:

Process O-A: Initially the material possesses no net polarization. As the electric field increases in magnitude domain growth takes place in preferentially aligned domains at the expense of neighbouring domains. However, when the electric field intensity increases above a certain threshold value the material experiences 180° ferroelectric domain switching. As the domains are progressively rotated to align with the electric field, the material reaches saturation polarization (P_S).

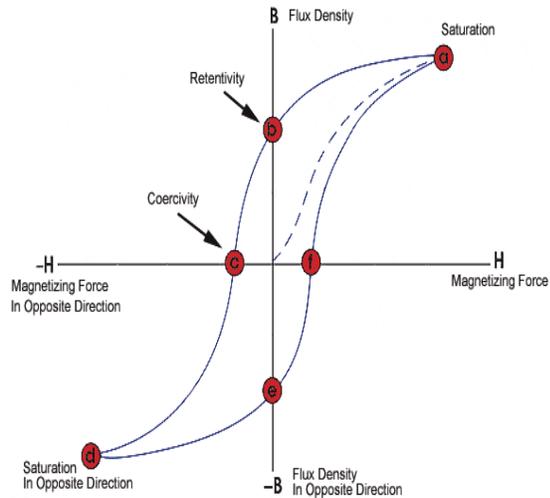


Fig. 2.8 P-E graph

Process A-B: Now as the electric field is lowered, the depolarization process does not follow its original path. Rather, the polarization decreases at a lower rate. Even when the electric field is completely removed, the material is still left with a large remnant polarization (P_r). This is a result of the polar domains being stuck in local minima which limits their tendency for back switching.

Process B-C: When an electric field is applied in a reverse direction, (P_r) slowly decreases. The electric field strength required to completely depolarize the material is termed as coercive electric field (E_C).

Process C-D: Again, when the electric field strength increases a trend similar to process O-A is observed.

Upon completing all the process (O-A-B-C-D-E-F-A) we obtain the full (P-E) hysteresis loop. It is to be noted that the loop is symmetrical and the hysteresis parameters viz. P_S , P_r and E_C remain the same in both directions. The area under the (P-E) loop signifies dielectric losses in the form of heat generated.

2.9 Literature collection relevant to the related study

Crystals having the general formula $(C_nH_{2n+1}NH_3)_2MCl_4$ with $n = 1,2,3$ and $M = Mn, Fe, Cd, Cu, Zn$ etc., were extensively studied in the past for their phase transition and their related phase mechanism [58-63]. The methylammonium crystals with $M = Cd, Mn, Fe$ and Cu of the family, C_nCdCl with $n = 1,2,3$ etc., are isostructural and show similar type of phase transition [64-67]. The organic cation of the type ethylammonium with tetrachlorometallates were studied for their phase transition related mechanisms [68]. These studies promptly conveyed that the transitions are essentially subjected to the nature of the organic cations used. The reason being is the reorientational motions of the organic cation in these type of crystals. Hence we thought of comparing the organic cations with metal anion of the type tetrachlorozincates. On the basis of their related phase transitions we thought of exploring the possibility of ferroelectric properties in these type of crystals. Also growing interest on ferroelectric materials based on their applications prompted this study. There are wide varieties of ferroelectric materials in the past classified under the categories inorganic, organic and semiorganic ferroelectric materials. Inorganic materials are mainly used for this application and in later days to till date inorganic ceramics also played crucial role in research addressing the ferroelectric properties of these materials. Preparation of these materials are cumbersome and defects present while preparation are some difficulties which may affect the properties to some extent. Organic ferroelectrics are still in the nascent stage and material stability and strength poses several limitations to this type of growth [69]. Hence we made an earnest attempt to grow semiorganic single crystals for this desired application. Moreover growing semiorganic single crystals doesn't require costly equipments and

the solution growth technique is a rather simple technique using which defect single crystals can be grown. These semiorganic single crystals are much stronger (mechanical and thermal stability) than their organic counter part.

Efforts made in this connection are discussed here. The molecular groups responsible for ferroelectric property has been attempted successfully in the present work based on the previous works. The properties of ethylammonium, methylammonium like cations and tetrahedral geometry based anions like tetrachlorozincate are found to be suitable candidates for addressing the ferroelectric property and hence used in the present study. In other words it means that some of the molecular groups that are responsible for the desired physical properties of the materials through which bandgap, insulating property etc., have been modified resulting ferroelectric nature. Hence there is a possibility of improved ferroelectric property. The inorganic cation and organic anion when combined on a single molecular scale produce new crystal structures with special and multi functional properties [70]. The distorted tetrahedral geometry of tetrachlorozincates in the formation of crystal structures with their counter cations which are responsible for the formation hydrogen bonding [71, 72]. This in turn may have the ability to modify the dipole- dipole interaction viz., the polarizability. Crystals of general formula $(NR_4)_2 MCl_4$ having divalent metal cation undergo different phase transition revealing many special physical properties. A possible transition from incommensurate to commensurate phases occur in such choices leading to ferroelectric property [73-79]. For example the onset of disorder in the methyl group of a crystal structure [80] results in phase transition, a possible modification in the crystal structure. Also phase transition in such crystal structures leads to ferroelectric

properties in commensurate phases [81]. These commensurate – incommensurate phases occurring in crystals having phase transition which are identified with dielectric permittivity, DC and AC electrical conductivities [82]. The occurrence of anomaly in such conductivities in different polar axis and the resulting variation in activation energy indicate the presence and disappearance of domain walls. This in turn speaks about the ferroelectric property. The anisotropy in electrical conduction found in such crystals reveals imperfections and dislocations in these types of single crystals [83]. The different types of Phase transition that occur in the materials can well be understood using Raman tool. Phase transition that occurs in molybdenum ditelluride between tetragonal to the monoclinic phase shows a hysteresis loop in Raman spectra. The original tetragonal phase of the crystal orientation is preserved and identified by the polarization resolved Raman spectroscopy while the material is in the induced monoclinic phase [84]. Structural phase change yield many material/physical properties based on the physics behind phase transitions leading to potential applications [85].

The possible Raman modes appear in the crystal geometry for various functional groups probe the structure of the compound as well as the symmetry that prevails in the structure. The phase evolution that occur in Meteo2 leading different lattice configurations are distinctly revealed by the phonons vibrational modes of Raman Spectroscopy. Also specific excitation wavelength yield large Raman intensity on monolayers [86].

Also the polarization mechanism involved in the geometry also can be well understood with the Raman tool. The non-linear behaviour of the polarization mechanism with respect to the electric field confirms the ferroelectric behaviour.

Moreover the polarization with respect to the frequency of the applied electric field give rise to the nature of polarization such dipolar, orientational, electronic etc., Understanding of the types of polarization and its appearance in the given geometry decides the type of application that it undergo. Understanding of the phonon modes also would be of high use in deciding the types of interaction and also about the domain structure. Raman tools are widely used for the above purpose. The occurrence of domain and the nature domain walls explain the possibility of ferroelectric behaviour in the materials. Polarization microscopes are available to probe the types of domain and also provide information about the nature of domain walls. Conductivity and dielectric permittivity measurements also can provide information about the domains and its walls.